Review

A critical review of selenium analysis in natural water samples

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A R T I C L E   I N F O

A B S T R A C T

This paper critically reviews the current understanding of the analysis of selenium in the natural environment. Several inorganic species of Se (-2, 0, $+4$, and $+6$) and organic species (monomethylated and dimethylated) have been reported in aquatic systems. Inorganic speciation of Se varies with pH and E_h. Many different analytical methods including UV–visible spectrophotometry, spectrofluorimetry, atomic fluorescence spectroscopy (AFS), chromatography, flameless atomic absorption spectroscopy (FAAS), electrochemistry, and inductively coupled plasma with atomic emission (ICP-AES) or mass spectrometry (ICP-MS) are available for quantification of selenium levels in different matrices. In recent years, analytical speciation techniques made a great leap in separating and detecting low levels of Se, but analyzing reduced species such as Se(0), polyselenides, and sulfur–selenium mixed species in the environment need further development. A number of selenium compounds has been identified in biota, but positive identification of such compounds in environmental samples is needed to understand the speciation of selenium in natural waters, sediments, and soils.

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1. Introduction

The narrow concentration range between essentiality and toxicity for Se and adverse effects for fish and wildlife populations experienced in many world regions require a thorough understanding of processes responsible for Se mobilization. The complex speciation of Se, which is governed by biological processes

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occurring at the sediment and in the water column as well as by physicochemical factors including redox conditions, pH and availability of sorbing surfaces [1,2], makes the analysis of selenium species more important than total selenium itself. The most relevant species include Se(VI), Se(IV), Se(0), Se(-II) and a number of Se-containing organic compounds [1]. Selenium is reduced to hydrogen selenide, H_2Se, or other selenides at relatively low redox potentials. Hydrogen selenide by itself is not expected to exist in the aquatic environment since the Se(0)/H_2Se couple falls even below the H^+/H_2 couple. Aqueous solutions of H_2Se are actually unstable in air due to its decomposition into elemental selenium and water. Under moderately reducing conditions, heavy metals are precipitated as the selenides, which have extremely low solubilities. The following are log Ks values of some heavy metal selenides of environmental interest: −11.5 (Mn^{2+}), −26.0 (Fe^{2+}), −60.8 (Cu^+), −48.1 (Cu^{2+}), −29.4 (Zn^{2+}), −35.2 (Cd^{2+}), and −64.5 (Hg^{2+}). The precipitation of selenium as heavy metal selenides can be an important factor affecting the cycling of the element in soils and natural waters.

2. Analysis

A strong interest in the dual role of Se as an essential element and a toxic one led to the development of various analytical techniques for the determination of selenium species in environmental matrices [3–10]. The evaluation of the role of elemental selenium in the speciation of this element is a critical point, due to the difficulty in the detection of Se(0) at environmental concentrations. Se(0) is commonly considered an unavailable form of Se because of its insolubility and its presence as a colloidal species, which represents a criticity in the separation of selenium species. More recently, Se(0) was determined in sediments by using X-ray based techniques, including X-ray absorption and X-ray fluorescence spectroscopy [11–13]. Although in recent years the performances of analytical speciation techniques have been greatly improved providing both good separation and powerful detection levels, quantitative evaluation of the speciation of Se in the environment still presents many challenges, particularly in reducing environments [10,12,14]. Recent studies seem to suggest that Se(0) is one of the largest pools of Se in aquatic systems since it may account for about 30–60% of total Se in sediments [9,15].

2.1. Atomic absorption and atomic fluorescence spectroscopy

Flameless atomic absorption spectroscopy (FAAS) has been employed with three main configurations [4]: electrothermal atomization with direct sample injection in a graphite furnace (ETAAS) [16], hydride generation with quartz tube atomization (HG-AAS) and hydride generation with in situ trapping in a graphite furnace (HG-ETAAS). HG-AAS and HG-ETAAS offer reduced chemical interferences but require larger sample volumes than does ETAAS. HG-ETAAS including pretreatment with an iridium coating, represents an elegant and reliable technique for the determination of Se and other elements such as Te, and As, allowing preconcentration and better control of interferences both in the liquid phase and in the atomization step [4]. When coupled with a flow injection technique, the detection limit is at the $ng\,L^{-1}$ level (Fig. 1).

Sodium borohydride ($NaBH_4$) is the most common reducing agent used to obtain Se hydride species. Se(IV) is the only species able to produce hydrides, thus the sample analyzed without any pretreatment provides the Se(IV) concentration. Total inorganic selenium in the sample may be obtained after a preliminary reduction of Se(VI) to Se(IV) by reaction with $NaBH_4$, HBr, $HBr/KBrO_3$, HCl or HCl/KBr at high temperature [17]. UV photolysis in alkaline or acid solution is also used for the reduction of Se(VI) to Se(IV) [18]. The more traditional approach consists of heating the sample with 2–6 M HCl in a microwave oven at 90–100 °C for 20–45 min. In the case of samples containing Se(-II), oxidation to Se(IV) with 0.04 M potassium peroxodisulfate solution in HCl solution is possible. Hydride generation atomic absorption spectroscopy (HGAAS) using quartz tube atomization was recently applied to determine the concentration of Se(IV) in several Se(IV)-reductant systems [19–21]. Measurements were preceded by tests proving that Se (0) was kinetically unable to develop hydrogen selenide by reaction with sodium borohydride [20]. To prove the inability of red Se(0) to react with sodium borohydride forming hydrogen selenide, we monitored the HGAAS response during the reaction of Se(IV) with ascorbic acid at pH 2. The decrease of the analytical response during the reaction was a clear indication that Se(0) produced by the reduction with ascorbic acid did not respond to the HGAAS analysis and, upon completion of the reaction, no analytical response was obtained. These results proved that Se(0) was not determined by HGAAS under our experimental conditions, in agreement with similar evidences [22]. Therefore, the selenide developed in the HGAAS system reflects the concentration of residual selenite present in the sample.

Among the studied reductants (hydrogen sulfide, cysteine, and ascorbic acid), hydrogen sulfide interfered in the analysis of Se(IV) using HGAAS. As shown in Fig. 2, the peak area decreased with increase in the concentration of hydrogen sulfide. This interference could be eliminated by diluting the concentration of sulfide below
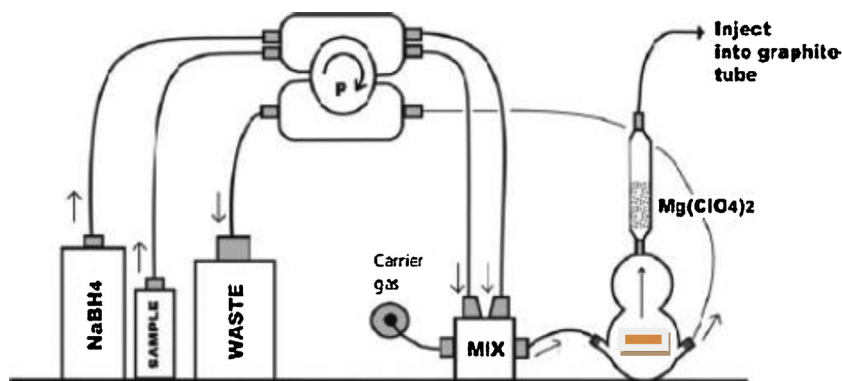

Fig. 1. Schematic representation of the flow injection system and the hydride generation chamber ▬ (adapted from Pettine et al. [28] with the permission of Elsevier Inc.).
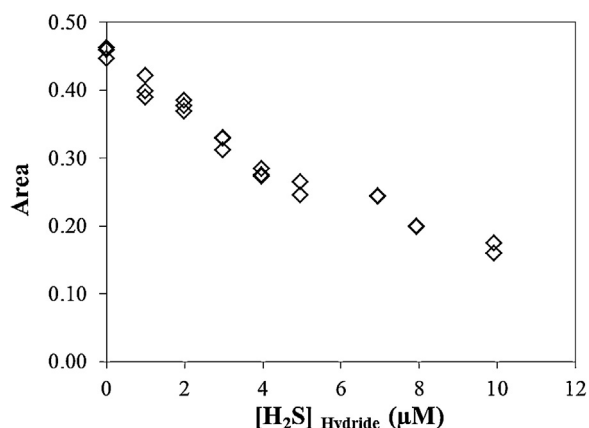
Fig. 2. The effect of sulfide concentrations on the HGAAS determination of 78.96 ng selenite (purging time before the addition of sodium borohydride = 25 s) (adapted from Pettine et al. [20] with the permission of Elsevier Inc.).

Fig. 4. Enhancement factor for As ($\bullet$), Se ($\triangledown$) and Hg ($\blacksquare$) as a function of bicarbonate concentration (adapted from Pettine et al. [28] with the permission of Elsevier Inc.).

$2 \mu M$. Concentrations higher than $2 \mu M$ would require removal of sulfide prior to analysis of Se(IV). The precipitation of sulfide anion by adding Cu(II) resulted in removal of the sulfide in the Se(IV)-hydrogen sulfide mixed solution [20]. The low solubility product constants of copper sulfides (Cu_2S and CuS) ensured the precipitation. However, residual Cu^{2+} in solution may be responsible for a decrease in the analytical answer by Se(IV) (Fig. 3). Ascorbic acid ($<500 \mu M$) and cysteine ($<60 \mu M$) did not interfere with determining the concentrations of Se(IV) using HGAAS [19,21].

Atomic fluorescence spectroscopy (AFS) is another spectroscopic method that has been used in the analysis of selenium [4,23]. AFS is well suited for coupling with HG using small hydrogen-argon diffusion flames as atomizers [24]. In the HG-AFS protocol proposed by Chen et al. [18], Se(IV) was directly measured in 3 M HCl, while Se (IV)+organic selenium was measured after UV irradiation for 2.5 h in a 1% (v/v) $HNO_3 - 2\%$ (v/v) HCl, and total selenium was measured after UV irradiation in 3 M HCl. The presence of a low concentration of HCl (2%, v/v) hinders further photo oxidation of Se(IV) to Se(VI) during the photolysis treatment [18].

2.2. Plasmic spectrometric methods

Extensive applications of inductively coupled plasmic spectrometric methods for Se analysis with atomic emission (ICP-AES) or
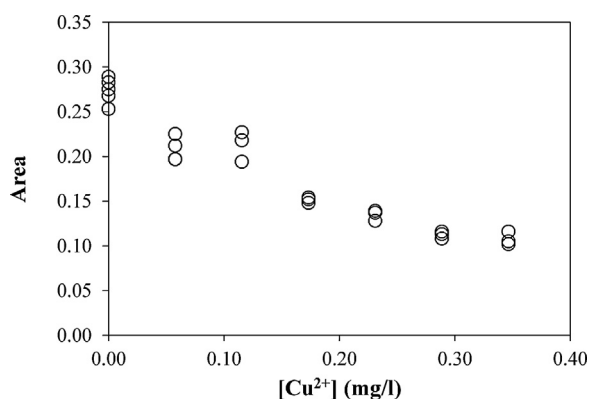

Fig. 3. The effect of Cu^{2+} concentrations on the HGAAS determination of 78.96 ng selenite (purging time before the addition of sodium borohydride = 25 s) (adapted from Pettine et al. [20] with the permission of Elsevier Inc.).
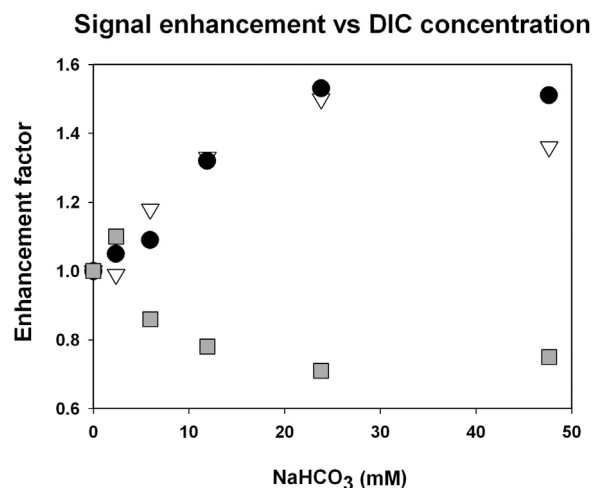
mass spectrometry (ICP-MS) have been reported [6,25,27]. In ICP-MS, all the selenium isotopes (^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, and ^{82}Se) are influenced by isobaric or polyatomic interferences. While the natural abundance of mass number 74 for selenium is the lowest (less than 1%) and is of too low abundance to be used for analytical determinations, Se mass number 80, which is by far the largest (49.6%), is affected by a large ^{40}Ar$_2^+$ interference. Other less abundant isotopes of selenium, such as ^{82}Se (9.2%), ^{78}Se (23.5%), ^{77}Se (7.6%), or ^{76}Se (9.3%,), have fewer polyatomic interferences from the plasma and are usually monitored [27]. The use of a collision/reaction cell, operating with hydrogen gas, lowers argon dimer interferences with selenium but may give rise to polyatomic interferences in the presence of bromide (such as ^{79}Br^{1}H$^+$ and ^{81}Br^{1}H$^+$) causing overestimation of ^{80}Se or ^{82}Se. The use of deuterium as a collision/reaction gas removes this type of interference. Non-spectroscopic interferences originating from the sample matrix may also cause either an enhancement or a depression of the analytical signal by influencing sample transport, ionization in the plasma, ion extraction or ion throughput in the resultant ion beam [25]. The presence of carbon in the plasma may affect ICP-MS measurements giving both spectral and matrix interferences. Carbon gives rise to molecular interfering species whose effects may be minimized by using a collision or dynamic reaction cell. Matrix effects induced by the presence of carbon consist of a signal enhancement caused by (a) charge transfer reaction from C+ species to analyte atoms, (b) improvement in the nebulisation of the sample, and (c) shift of the zone of maximum ion density in the plasma. Mechanism (a) operates for hard-to-ionize elements like Se and As having ionization potentials (9.75 and 9.82 eV, respectively) lower than carbon (11.36 eV). The ionization of Se and As is in the order of 33% and 52%, respectively, under usual ICP-MS conditions and may be significantly increased by the presence of organic or inorganic carbon, according to the chemical ionization process

$$C^+\text{-species} + M \rightarrow M^+ + C\text{-species} \tag{1}$$
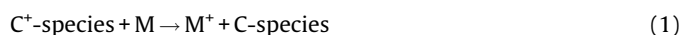
The high ionization potential of selenium often requires the addition of carbon compounds such as methanol, ethanol, etc. to samples, standards and blanks to increase sensitivity (Table 1). Elements with ionization energy much lower than carbon do not show any significant effect attributable to reaction (1) since their ionization efficiency is close to 100% under usual conditions.

Table 1
Literature values of carbon-induced signal enhancement by ICP-MS in the presence of different organic compounds directly added to the sample, unless otherwise specified in the comments (adapted from Pettine et al. (2007) [28] with the permission of Elsevier Inc.).

Carbon source	mol CL^{-1}	Enhancement factor	Comments
Glycerol	3	6 for Hg; 3.25 for Au; 2.5 for Se; 2.4 for As; 1.9 for Te	RF = 1200 W; neb. gas = 0.85 L min^{-1}
Methane	–	5.3 for As and Se	RF = 1200 W; neb. gas = 0.7–0.75 L min^{-1}; methane added directly to Ar gas flow
Methanol	0.74	3.4 for As and Se	RF = 1320 W; neb. gas = 1.00 L min^{-1} (var)
Methanol	15	8.5 for As; 3.0 for Se; 3.0 for Hg	FI RF = 1200 W; neb. gas = 0.7–0.75 L min^{-1}
Ethanol	17.1	8.0 for As; 3.0 for Se; 3.0 for Hg	FI RF = 1200 W; neb. gas = 0.73–0.805 L min^{-1}
1-Propanol	20.0	7.5 for As; 3.0 for Se; 5.0 for Hg	FI RF = 1200 W; neb. gas = 0.75–0.805 L min^{-1}
Mannitol (Ma)	0.49 (Ma)	3.8–5.0 for As; 1.9–2.9 for Se; 0.2–0.7 for Ge	RF = 1300–1500 W; Babington nebulizer; neb. gas = 1.0–1.05 L min^{-1}
Ethanol (E)	0.34 (E)		
Methanol (M)	0.25 (M)		
Glucose	0.67	2.5 for As; 2.4 for Se; 2.0 for Zn	RF = 1300 and 1500 W; Babington nebulizer; neb. gas = 1.0–1.05 L min^{-1}
Ammonium acetate	0.52	2.4 for As; 2.3 for Se; 1.9 for Zn	RF = 1300 and 1500 W; Babington nebulizer; neb. gas = 1.0–1.05 L min^{-1}
TRIS	0.66	2.2 for As; 2.0 for Se; 1.8 for Zn	RF = 1300 and 1500 W; Babington nebulizer; neb. gas = 1.0–1.05 L min^{-1}
Acetonitrile	0.24	4.3 for As; 4.0 for Se; 2.4 for Zn	RF = 1300 and 1500 W; Babington nebulizer; neb. gas = 1.0–1.05 L min^{-1}
Methanol	0.16	4.1 for As; 3.9 for Se; 2.3 for Zn	RF = 1300 and 1500 W; Babington nebulizer; neb. gas = 1.0–1.05 L min^{-1}
Methanol	0.25	1.8 for As; 1.6 for Se; 1.4 for Zn	RF = 1150 W; neb. gas = 0.75 L min^{-1}
Methanol	0.50	4.5 for As; 4.0 for Se; 2.8 for Zn	RF = 1350 W; neb. gas = 0.78 L min^{-1}
Methanol	2.5	3.5 for As; 3.0 for Se; 1.8 for Hg	RF = 1300 W; Babington nebulizer; neb. gas = 1.05 L min^{-1}; organic solvent added directly into spray chamber
Acetone	1	4.0 for As and Se; 1.8 for Hg	RF = 1300 W; Babington nebulizer; neb. gas = 1.05 L min^{-1}; organic solvent added directly into spray chamber
Acetic acid	15	3.1 for Hg; 2.9 for Se; 0.2 for Hg	RF = 1300 W; Babington nebulizer; neb. gas = 1.05 L min^{-1}; organic solvent added directly into spray chamber
Methanol	5	31 for As and Mg; 17 for Co; 12 for Rh; 6 for Se and Pb	RF = 1300 W; low flow parallel path nebulizer Mira; MIST CE neb. gas = 1.05 L min^{-1}

With the aim of clarifying the different results obtained in CO$_2$ rich mineral waters by two independent techniques (Octopole Reaction System Inductively Coupled Plasma Mass Spectrometry, ORS-ICP-MS, and Flow Injection Hydride Generation Electrothermal Atomic Absorption Spectrometry, FI-HG ETAAS) we measured (Fig. 4) the ORS-ICP-MS signal enhancement of sodium bicarbonate artificial solutions (0; 2.38; 5.95; 11.90; 23.81; 47.62 mM DIC) with 0.667 μM As, 0.127 μM Se and 0.050 μM Hg, previously acidified with 1% (v/v) HNO$_3$ [28]. Se determinations by FI-HG ETAAS are in case of water solutions rich of organic and inorganic carbon more accurate than those by ORS-ICP-MS.

2.3. Spectrophotometric methods

Only a few of the reported spectrophotometric methods have sufficient sensitivity and selectivity for trace levels of selenium in environmental matrices. The reagent, 6-amino-1-naphtolo-sulphonic acid, forms a yellow complex absorbing at 392 nm, with a detection limit of 80 μg/L [29]. Se(IV) reacts with 2,3-diamine-naphthalene or 3,3′-diaminebenzidin (DAB) in acidic matrices to form complexes that can be extracted by cyclohexane or toluene that are characterized by absorption maxima at 378.5 and at 420 nm, respectively, with similar detection limits of about 10 μg/L [29,30]. A turn-on fluorescent probe for Se(IV) has recently been described which consists of a silica nanoparticle core which is coated with Se(IV)-induced fluorescent molecules [31].

Catalytic-kinetic spectrophotometric methods are an attractive alternative for the determination of trace amounts of selenium. Se(IV) catalyzes the reduction of maxilon blue-SG or sulfonazo by sulfide [32], and the reduction of methylene blue by selenosulphides [33], which give rise to a decrease in absorbance that is dependent on Se(IV) concentration. Se(IV) also catalyzes reactions producing an absorbance increase, such as: the photooxidative coupling of *p*-hydrazinobenzenesulfonic acid with *N*-(1-naphthyl) ethylendiamine to form an azo dye absorbing at 538 nm [34], and the reaction of EDTA and sodium nitrate with

ammonium iron(II) sulfate hexahydrate in acidic media [35]. Chung et al. [36] used the reaction of 4,4′-dichloro(3-mercapto-1,5-diphenylformazan) with Se(IV) in 2 M HCl samples to form a yellow–red-colored complex [36], which may be extracted quantitatively into *n*-hexane and has a detection limit of 10 μg/L. Matamoros and Benning [37] used the reaction of Se(IV) ions with hydroxylamine hydrochloride, which in turn diazotizes *p*-nitroaniline and is coupled with *N*-1-naphthyl-ethylenediamine dihydrochloride (NEDA), to form a red colored azo compound with a detection limit of 10 μg/L. Chand and Prasad [38] recently proposed a method based on the catalytic effect of Se(IV) on the reduction of bromate by hydrazine dihydrochloride in acidic media and the consequential oxidation/decolorization of methyl orange (MO) by the generated bromine. Afkhami and Madrakian [39] used this MO based method after a preconcentration of elemental selenium on activated carbon. Total inorganic Se may be determined after Se(VI) reduction to Se(IV) following pH adjustment.

2.4. Electroanalytical methods

Electroanalytical techniques are able to determine traces of Se (IV), while the reduction of Se(VI) to Se(IV) requires a very positive standard potential and is so slow that no faradaic current is observed in the usual voltammetric experiments [40]. Se(VI) may be determined after its preliminary reduction to Se(IV). Cathodic stripping voltammetry (CSV) with a hanging mercury drop electrode (HMDE) or a thin mercury film electrode as the working electrode is often used. Selenium is accumulated by electroreduction either in the form of HgSe [41,42] or as intermetallic compounds, such as copper-selenium and rhodium–selenium, when copper or rhodium are added to the samples [43]. Selenium can also be determined by CSV after adsorptive collection in the form of complexes with 3,3′-diaminobenzidine on an HMDE [44]. Bertolino et al. [45] preconcentrated reduced elemental selenium on activated carbon from natural waters, then oxidized Se(0) with

bromate in acidic media and indirectly determined it through bromide formation using Osteryoung square-wave voltammetry (OSWV). Ashournia and Aliakbar [46] recently proposed two methods based on adsorptive self-accumulation of Se-I$_2$ and 5-nitropiazselenol (both giving a higher efficiency of absorption compared to Se(IV) alone) on a thin mercury film electrode followed by differential pulse CSV. Since the accumulation process in both cases was carried out without applying potential, the possibility of interfering compounds was minimized. The adsorbed Se-I$_2$ or 5-nitropiazselenol were then stripped in a separate 0.05 M HCl solution by DPC potential scans, which reduced adsorbed Se(0) to Se(-II) in the first case and mercury selenide to elemental mercury and hydrogen selenide in the latter case. Zhang et al. [47] used adsorptive stripping voltammetry at a bismuth coated glassy carbon electrode of the complex Se(IV)–(ABSA)$_2$, produced by the reaction of Se(IV) with *p*-aminobenzene sulfonic acid (ABSA) at pH 2.9. The addition of Amberlite XAD-7 resin directly in the voltammetric vessel was used to remove organic matter (OM) during the deoxygenation phase of samples containing high OM concentrations, followed by accumulation of Cu$_2$Se on an HMDE [48].

2.5. Other techniques

Neutron activation analysis (NAA), fluorimetry and gas-chromatography (GC) have also been used for the analysis of selenium. Recently, Sun and Yang [49] proposed a method for the simultaneous determination of reduced and oxidized species of As, Se and Sb in natural waters. Se(IV), As(III) and Sb(III) were coprecipitated with lead pyrrolidinedithiocarbamate (Pb(PDC)$_2$) from pH 2.0 to 4.0 while quantitative coprecipitation of Se(VI), As (V) and Sb(V) were achieved by reduction with titanium(III) chloride followed by Pb(PDC)$_2$ coprecipitation at pH 4.0. Precipitates were collected on 0.45 μm membrane filters, dried and inserted into polyethylene vials and sealed for neutron irradiation in a Tsing-Hua Open Pool Reactor (THOR). The radiotracers ^{75}Se, ^{76}As and ^{124}Sb, were used for the determination, resulting in detection limits of 1 ng L^{-1} for Se and As and 0.1 ng L^{-1} for Sb.

Piazselenol derivatives produced by reaction of selenium(IV) with aromatic ortho-diamines can be used for the determination of selenium by gas-chromatography or fluorimetry [25]. GC techniques use either packed glass columns or capillary columns and electron-capture based detectors [25]. GC was also used for the separation of selenoamino acids after their conversion into less polar, more volatile derivatives such as trimethylsilyl derivatives [25]. The reagent ethyl chloroformate was used for the simultaneous derivatization of selenomethionine, selenoethionine and selenocysteine and their separation by capillary GC by Janák et al. [26]. Derivatization of Se(IV) with 2,3-diaminonaphtalene (DAN) and some of its halogenated derivatives to give the corresponding 4,5-benzopiazselenol was used for determination of selenium by fluorometric detectors [25].

2.6. Hyphenated techniques

Hyphenated techniques couple two (or more) independent techniques for the separation and analysis of selenium species [6,50]. Chen and Belzile [8] reviewed the most recent applications of HPLC combined with hydride generation or chemical vapor generation and atomic fluorescence spectroscopy (HPLC-HG/CVG-AFS) for the determination and speciation of As, Se, Sb and Hg. Morales et al. [7] reviewed the use of capillary electrophoresis (CE) as a separation technique for the analysis of selenium in different matrices including biological samples (plants and organisms), biological fluids (urine, human milk), and environmental samples.

CE was coupled with UV and fluorescence detection systems, ICP-AES and ICP-MS [51,52]. A routine IC-ICP-MS method for the determination of inorganic selenium species in microbial-treated industrial waste water was developed [27]. They compared the performance of two different anion exchange resins (ANX 3206 by Cetac and As 10 by Dionex) for the separation of Se(VI) and Se(IV). Vassileva et al. [53] proposed an IC-ICP-MS procedure for the separation and determination of As and Se species in groundwater and extracts of contaminated soils with detection limits <1 μg L^{-1} for the various As species and approximately 4 μg L^{-1} for Se(IV and VI). It was possible to increase the number of separated selenium compounds from two inorganic species (Se(IV) and Se(VI)), to several organic compounds in a single chromatographic run by using anion-exchange or silica-based cation-exchange columns [50]. The application of ion-pair reversed-phase chromatography with appropriate counter ions has increased considerably in recent years due to its capacity of simultaneous separation of anionic, cationic and neutral species.

2.7. Selenium speciation in soil

Sequential extraction procedures applied to soil or sediment [5,54,55]. Tolu et al. [56] are able to differentiate soluble Se, ligand-exchangeable Se, tightly sorbed Se, elemental Se, Se substituted in a carbonate matrix, nonextractable metal selenides and organo-Se compounds. Sequential extractions, however, are operationally defined and results may be inaccurate [57]. Recently, Weng et al. [58] used the anion Donnan membrane technique (DMT) to analyze the speciation of Se in the 0.01 M CaCl$_2$ extractions of grassland soils by ICP-MS and stressed the advantage of using DMT to separate colloidal particles in the sample from dissolved species. The results revealed that most of the Se in the extracts (67–86%) was colloidal-sized Se. These findings suggest a discrepancy with previous results [59] suggesting that inorganic selenate was the dominant species in agricultural drainage waters and organic Se was <10%.

A number of X-ray based techniques including, X-ray absorption and X-ray fluorescence spectroscopy (XAS and XRF), applied at macroscale and microscale levels, may provide information on the speciation of selenium in soil and sediment [11–13]. Comparative analysis between sequential extractions and X-ray based techniques occasionally pointed out serious differences in the determination of reduced selenium species such as Se(0).

3. Concluding remarks

Many different analytical methods for quantification of selenium levels are available (Table 2). Electroanalytical systems, and hydride generation or other derivatization systems (ethylation, piazselenole formation) are selective for Se(IV). The analysis of other redox species of Se based on the above techniques requires a preliminary conversion of Se(VI), Se(0) and Se(-II) species to Se(IV). The use of ETAAS, AFS or plasmic spectrometric methods may quantify total selenium. Hyphenated techniques that couple separation techniques (size exclusion, ion-exchange and reversed phase chromatography, capillary electrophoresis etc.) with advanced detection systems (MS, FAAS, ICP-AES, ICP-MS) have been employed for evaluation of selenium speciation in aqueous solutions. The above separation techniques have often been coupled with ICP-MS allowing simultaneous determination of several inorganic and organic Se species and in some cases the contemporary determination of species of other elements such as arsenic and antimony. Gas chromatography coupled with ICP-MS has been used to separate and detect volatile Se species. Although in recent years the performance of analytical speciation techniques has been greatly improved providing both good separation and

Table 2

Techniques for total selenium analysis and Se speciation and related detection limit.

Technique	Se species determined	Typical instrumental detection limit (µg/L)	Comments
ORS-ICP-MS	A	0.01	The use of a collision reaction cell (ORS) lowers isobaric and polyatomic interferences, but possible spectroscopic interferences due to the matrix (i.e. carbon).
ICP-MS	A	0.1	Subject to isobaric, polyatomic and matrix interferences.
HG-ETAAS	A	0.005	Hydride generation coupled with *in situ* trapping of hydrides in a graphite atomizer pretreated with iridium is highly selective for Se(IV). Se(VI), Se(0) and most organoselenium species must be converted to Se(IV).
HG-AAS HG-AFS	Se(IV)	0.1	Hydride generation may be coupled with AAS or AFS to determine Se(IV); other Se species should be converted to Se(IV).
ETAAS	A	1	Metal modifiers are needed for thermal stabilization of the analyte.
HMDE-CSV	Se(IV)	0.05–0.5	Se(IV) may be accumulated by electroreduction in the form of HgSe, SeI$_2$. or as Se complexes; other Se species should be converted to Se(IV).
NAA	Se(IV) or Se (IV) + Se(VI)	0.001	Based on coprecipitation of Se(IV); Se(VI) may be eventually reduced to Se(IV) prior to coprecipitation.
Spectrophotometric methods	Se(IV)	10–100	Based on two different principles: (a) complexation, eventually followed by extraction in organic solvents; (b) catalytic-kinetic metods.
Hyphenated techniques	Se speciation	0.2–10	Two (or more) independent techniques allow the separation and analysis of Se species. HPLC, CE or IC were in most cases used for the separation step.

"A" include both inorganic and organic selenium.

powerful detection levels, quantitative evaluation of the speciation of Se in the environment still presents many challenges, particularly in reducing environments. The presence of some reduced Se species, such as Se(0), polyselenides, and sulfur–selenium mixed species is still questioned. Determination of such species is difficult due to the unavailability of certified standards and their inclusion in colloidal species, which could not be easily separated. Sequential extraction protocols are commonly used to assess selenium fractionation in sediments, although data interpretation can be biased by unselective extraction of targeted species and artifacts introduced during the extraction. The quantification of elemental selenium in particular is hindered by major discrepancies with results from nondestructive XANES techniques, pointing out that the analysis of this species of selenium is at present a major difficulty in aqueous and solid matrices.

Acknowledgment

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